

KINETICS OF THE WATER ABSORPTION IN SLAG CEMENT MORTARS.

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Abstract

We study the kinetics of absorption of water in portland cement mortars added with 60, 70 and 80% of granulated blast furnace slag (GGBS or SLAG) cured in water and at open air and preheating at 50 and 100⁰C. A mathematical model is presented that allows describing the process not only in early ages where the capillary sorption is predominant but also for later and large times where the diffusive processes through the finer and gel pores are considered. The fitting of the model by computerized methods enables us to determine the parameters that characterize the process: i. e. the sorptivity coefficient (S) and diffusion coefficient (D). This allows the description of the process for all times and offers the possibility to know the contributions of both, the diffusive and capillary processes. The results show the influence of the curing regime and the preheating temperature on the behavior of GGBS mortars.

Keywords: Water transport, modeling, capillarity, diffusion, GGBS mortars.

1 Introduction

The role of water in the mechanism of deterioration of porous building materials has been recognized for a long time. The conjugate action of mechanical and chemical damages arising for instance from freeze/thaw cycles, shrinkage-induced cracking, salt crystallization and leaching [1] may lead to rapid degradation of the bulk mechanical properties of building materials and significantly reduce the service life of constructions.

The durability of building structures is thus critically determined by the rate at which water infiltrate and move through the porous structure. In addition the penetration of water in building materials provides a mechanism and path for the penetration of deleterious materials like chloride and sulfate ions which can lead to the corrosion of steel reinforcement in concretes [2, 3, 4, 5, 6]. Sorptivity and diffusion are the primary mechanisms that control the transport of deleterious materials inside of the concrete [7]. The diffusion corresponds to the ionic movement under the action of a concentration gradient (it occurs fundamentally when the material is dampened) and sorptivity is the property that characterizes the disposition of a porous material of absorbing and to transmit water by capillarity.

Because of its economic implications, the problem of water movements in porous building materials has received great attention in the past and also at present. A better understanding of the water absorption and moisture transfer can therefore reduce or prevent damage in building materials. For that reason these phenomena are of interest to physicist and engineers.

This phenomenon has been the object of intensive research [7, 8, 9, 10, 11, 12, 13, 14, 15, 16] where different methods of measuring the uptake and movement of water in these materials (gravimetry, microwave method, electrical conductivity, relative humidity, ultrasonic method, nuclear magnetic resonance, etc) have been used.

It is known that the use of finely divided siliceous materials (such as fly ash, ground granulated blast furnace (GGBS or slag), rice husk ash, silica fume, etc) in concrete is the most direct, technically feasible and economically attractive solution to the problem of reinforced concrete durability.

In particular, these materials greatly improve the durability of concrete through control of high thermal gradients, pore refinement, depletion of cement alkalis and the capability for continued long-term hydration or pozzolanic reaction [17]. In developing countries where the increasing demand for construction take place, the technical advantages of pozzolans and slag in concrete are complemented by other economic, ecological and environmental considerations. These materials reduce substantially not only the energy consumption in the production of concrete, but also help to reduce environmental pollution through reduced emission of carbon dioxide.

Slag is a by-product from the production of steel. During production liquid slag is rapidly quenched from a high temperature by immersion in water [18]. The slag is a glassy, granular, non-metallic product that consists essentially of silicates and aluminosilicates of calcium and other bases [19].

The addition of slag (GGBS) diminishes the large pores and reduces porosity. It is due to the hydration of slag [20] which reacts with calcium hydroxide (originated during the hydration of portland cement) to form calcium silicate hydrate (CSH) gel with very small pore size. Thereby the slag increase the strength of the concrete product, which is more marked with the duration of exposure in comparison with the concrete based on ordinary portland cement OPC [21, 22, 23, 24].

Ho et. al. [25] showed that concrete quality with response to interrupted curing is improved by the incorporation of slag in concrete. The rate of water absorption by capillary action is significantly decreased when slag is used. GGBS concrete is substantially more resistant to chloride diffusion than portland cement concrete of the same strength grade. The uses of slag will considerable increase the service life of structures exposed to chloride environment and to provide sufficient cover to the steel reinforcement. Swamy has presented a critical and valuable evaluation about the use of slag in concrete [17].

From the scientific point of view and for numerous applications, simple but accurate models describing the water transport in mortars and concretes are important. Several models (which involve both analytical and numerical models) have been developed for describing this phenomenon in mortars and concretes without and with additions [7, 11, 26, 27, 28, 29], but they do not always agree with the experimental results. Several researchers describe the water absorption in concrete in early ages where the process of capillary absorption prevails but they don't describe the complete process where the moisture diffusion through the finer or gel pores may be considered. These finer pores increase its importance with time [7]. A model that considers both the capillary and diffusion phenomenon and allows us to explain the process for all ages will be of great importance.

The goal of the present paper is to develop a mathematical model for describing the water transport in GGBS cement mortars. The model proposed here consider that the capillary sorption and diffusion are the principal mechanisms to the absorption of water in slag cement mortars but this don't consider for simplicity an for having a less contribution other mechanism such as permeation, osmosis, thermal migration, etc that can be present. This model allows us to describe the process for early and large times. This gives the possibility of to know the contributions of the diffusion and capillary action in the water transport in cement mortars, which is very useful to predict the penetration of chloride or other ions that deteriorate the steel reinforcement in concretes. The fitting of the model by computerized methods lets us determine process parameters, such as sorptivity coefficient and diffusion coefficient. It allows us to characterize the kinetics of the water transport in GGBS cement mortars with 60, 70 and 80% of slag. Besides, the influence on the water sorption process of different curing regimes (curing in water and at open air) as well as the effect of changing the preheating temperature is analyzed.

2 EXPERIMENTAL

The experimental data presented in this paper were obtained from Mejias and Talero [22, 23].

The samples used correspond to cylindrical mortars (with a diameter and height of 50.8 and 50 mm respectively) manufactured with OPC (Table 1) blended with GGBS additions of 60, 70 and 80% by weight. A curing under water and at open air by 15 days was used and a posterior preconditioning of the samples at 100°C during 6h and cooling in desiccator for 24 h was applied. Other samples cured under water were dried at 50°C during 48 h and cooling in desiccator. Table 2 shows the general data for the samples.

Cement	SC_3	SC_2	AC_3	FAC_4
OPC	46.95	19.98	14.69	5.33

Table 1. Chemical composition of the OPC.

One of the ends of the samples was placed on a thin sponge (3 mm) to absorb water. The weight of the specimens was measured intermittently for about two weeks. Figures 1 and 2 show a scheme of the sorption test and the cumulative water absorption versus square root of time respectively.

Sample designations	Compositions	Curing regime (15 days)	Preconditioning temperature
S80W100	OPC + 80% slag	Water	100°C
S70W100	OPC + 70% slag	Water	100°C
S60W100	OPC + 60% slag	Water	100°C
S80W50	OPC + 80% slag	Water	50°C
S80A100	OPC + 80% slag	Air	100°C

Table 2. General data for the samples.

3 Formulation of the problem

The process of water transport in concrete has been studied by many researchers. In most of the cases has been possible to explain the process satisfactorily for early ages in

dry samples and without additions. It is frequently found that if a mortar or concrete surface is exposed to wetting by water then the cumulative water absorption (normalized to the exposed surface area) M/A (in kg/m^2) is proportional, during the initial absorption period, to the square root of elapsed wetting time t : [11]

$$\frac{M}{A} = St^{\frac{1}{2}} \quad (1)$$

where S is the sorptivity coefficient measured in $kg/m^2.h^{\frac{1}{2}}$. It is easily determined from the slope of the linear part of the M/A versus $t^{\frac{1}{2}}$ curve.

After a period of sorption the initial rate of ingress observed decreases as the water has accessed all the larger capillary pores. The decrease in gradient of the straight line portion of the water uptake versus square root of time indicates that sorptivity is now occurring via the finer pores and indicates the increasing importance of small pores with time [7]. Besides, some materials with extremely coarse pore structure experience little capillary suction and may show significant deviation from linearity after prolonged wetting.

It is widely known that in dry or partially dry mortars or concretes the predominant mechanism in the water absorption is the capillary suction (through the capillary pores) and when the time lapses, and the material begins to be saturated, the predominant mechanism is the diffusion (through the finer and gel pores) [7, 30].

However both processes should coexist simultaneously from early ages (a capillary process through the big capillary pores and a diffusive process through the small pores and gel pores) mainly in slag mortars or concretes where the quantity of gel pores increases and the big capillary pores decrease considerably.

To model the capillary and diffusive processes we consider that the cumulative water absorption with time in general can be expressed as:

$$\frac{M}{A} = St^{\frac{1}{2}} + \text{diffusive term} \quad (2)$$

the first term on the right can be written as [7]:

$$N\rho\{1 - \exp(\frac{-St^{\frac{1}{2}}}{N\rho})\} \quad (3)$$

where N is a constant related to the distance from the concrete surface over which capillary pores control the initial sorption and ρ is density of the water. This term was constructed so that at early ages, in the limit $t^{\frac{1}{2}} < \frac{N\rho}{S}$, expansion of the exponential

gives $N\rho\{1 - \exp(\frac{-St^{\frac{1}{2}}}{N\rho})\} \approx St^{\frac{1}{2}}$ which is the same as Eq. (1).

The diffusive term in (2) is obtained considering the physical diffusion of water and solving the continuity equation or second Fick's law, in non-stationary states with the initial and boundary conditions imposed by the given situation. The samples are cylindrical mortars, permeable only for a face with zero water (considering the water used in the test) as initial condition. In our case all the faces were sealed except the surface in contact with the water. Considering this geometry (Fig. 1) the diffusion problem is reduced to a unidirectional treatment where the diffusion coefficient D is assumed constant for each test.

The mathematical problem is given by the equation:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (4)$$

where C is the water concentration and t the time.

The initial and boundary conditions are given by:

$$C(x, 0) = 0 \text{ para } x \in (0, L) \quad (5)$$

$$C(0, t) = C_o \text{ para } t > 0 \quad (6)$$

$$\frac{\partial C}{\partial x} = 0 \text{ para } x = L \quad (7)$$

The first boundary condition (Eq. 6) shows the invariance of water concentration (C_o) in the surface for each sample.

The second boundary condition (Eq. 7) expresses the impermeability of the top of the sample in $x=L$.

In order to solve the boundary problem the Fourier method [31, 32] or the method of laplace transform [33] can be used. The result is:

$$C(x, t) = C_o \left\{ 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \exp\left(-\frac{(2n+1)^2 \pi^2 Dt}{4L^2}\right) \sin \frac{(2n+1)\pi x}{2L} \right\} \quad (8)$$

This solution expresses the water concentration profiles according to the (x) coordinate and the (t) time in all the section of the sample.

The amount of water absorbed through the area A of the permeable surface is:

$$M = \int \int \int_V C(x, t) dx dy dz \quad (9)$$

$$= AC_oL \left\{ 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 \pi^2 Dt}{4L^2}\right) \right\} \quad (10)$$

Therefore the amount per unit of area expressed in kg/m^2 is given by:

$$\frac{M}{A} = C_oL \left\{ 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 \pi^2 Dt}{4L^2}\right) \right\} \quad (11)$$

substituting the Eq. (11) as second term in Eq.(2), we obtain:

$$\frac{M}{A} = N\rho \left\{ 1 - \exp\left(-\frac{St^{\frac{1}{2}}}{N\rho}\right) \right\} + C_oL \left\{ 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 \pi^2 Dt}{4L^2}\right) \right\} \quad (12)$$

Eq. (12) represents a capillary-diffusive model. This expresses the mass of water per unit of area incorporated to the sample considering both, the capillary sorption through the large pores (first term) and water diffusion through the small pores and very finer gel pores (second term).

4 Results and Discussion

Fig. 2 shows the experimental results of the sorption test for the samples S80W100, S70W100, S60W100, S80W50 and S80A100. A quick decrease of the amount of water absorbed at early ages for all samples is appreciated, showing the samples S80A100 and S80W50 the biggest and smaller rate of absorption at early ages respectively. Later on the initial rate of ingress observed decreases (the water has accessed all the large capillary pores) until a stabilization of the curve (saturation) is reached for large times in dependence of the analyzed sample.

The samples S80W100, S70W100 and S60W100 with 60, 70 and 80% of slag show a

similar behavior. Big differences from the qualitative point of view are not appreciated. Qualitatively a bigger rate of initial sorption and bigger amount of incorporated water for long times is appreciated for the sample S80A100, followed by S60W100, S70W100 and S80W100. The sample S80W50 shows the smaller rate of initial sorption and the smaller amount of incorporated water for large times.

For samples curing at open air (S80A100) a greater rate of uptake of water is qualitatively appreciated in comparison with the samples (S80W100) curing under water. Also, the sample S80W50 preheating to 50°C shows a smaller sorptivity and amount of incorporated water that the sample S80W100 preheating to 100°C .

Shown in figures 3a, 3b, 3c, 4 and 5 are the cumulative water absorption (M/A) versus time (t) for S80W100, S70W100, S60W100, S80W50 and S80A100 samples. Solid lines represent the curves of the fitted model. The fitting of the model (Eq. (12)) permitted us to determine the parameters C, S, D and Co in each case. The values of these parameters for all samples are given in Table 3. In the figures the correlation (r) and multiple determination coefficient (R^2) are shown.

Mixture	Sorptivity coefficient S ($kg/m^2s^{\frac{1}{2}}$)	Diffusion coefficient D (m^2/s)	Co (kg/m^3)	N (m)
S80W100	$3, 16.10^{-2} \pm 0, 25.10^{-2}$	$1, 38.10^{-8} \pm 0, 08.10^{-8}$	$140, 52 \pm 5, 42$	$1, 51.10^{-3} \pm 0, 14.10^{-3}$
S70W100	$2, 75.10^{-2} \pm 0, 24.10^{-2}$	$2, 50.10^{-8} \pm 0, 23.10^{-8}$	$137, 34 \pm 8, 32$	$1, 52.10^{-3} \pm 0, 15.10^{-3}$
S60W100	$2, 81.10^{-2} \pm 0, 15.10^{-2}$	$6, 10.10^{-8} \pm 0, 27.10^{-8}$	$94, 62 \pm 3, 86$	$4, 02.10^{-3} \pm 0, 20.10^{-3}$
S80W50	$4, 80.10^{-3} \pm 0, 45.10^{-3}$	$2, 83.10^{-8} \pm 0, 14.10^{-8}$	$63, 75 \pm 3, 70$	$2, 17.10^{-3} \pm 0, 17.10^{-3}$
S80A100	$21, 31.10^{-2} \pm 2, 1.10^{-2}$	$1, 28.10^{-7} \pm 0, 08.10^{-7}$	$121, 52 \pm 6, 29$	$2, 75.10^{-3} \pm 0, 26.10^{-3}$

Tabla 3. Values of the parameters for all samples.

According with the values of the coefficients S and D the samples S80W100, S70W100, S60W100 with 60, 70 and 80% slag cured under water and preheating to 100°C show a similar behavior which agree with the qualitatively analysis carried out previously. The sample S80W100 curing in water shows a less sorptivity and diffusion (less S and D) in comparison with S80A100 curing at open air and therefore a bigger opposition to the uptake and water transport in the mortars. It is due to the influence of the curing regime on the pore structure. The curing in water facilitates the refinement of the pore structure in slag mortars and therefore leads to high degree of impermeability [21]. In other words, the lack of curing in water in slag cement mortars affects adversely the development of a very finer pore structure. On the other hand the curing at open air increase the absorption and porosity of slag cements [34, 35].

The changes in the diffusion coefficients (D) show the role of the diffusive processes, the importance of its consideration as well as their dependence with the structure of pores affected by the different curing regimes.

The results obtained for the samples S80W100 and S80W50 allows us to analyze the effect of the pre-conditioning temperature. A diminishing of the sorptivity S (see Table 3) is appreciated when diminish the pre-conditioning temperature. It is due fundamentally to strong role that plays the degree of saturation on the control of water uptake [7].

The water flows through the big capillary pores by action of the capillary force, being the flow rate determined by the pore structure and the local content of water. Therefore the capillary forces are bigger in dry materials as S80W100 (preheating at 100°C) that in partially dry materials as S80W50 (preheating at 50°C) and become minimum in completely saturated materials.

It should also be taken into account that for pre-conditioning temperatures around 100°C microcracking and other undesirable effects can be generated [23, 34], which contributes to a bigger capillary suction.

The variation of the diffusion coefficients D with the preconditioning temperature is not significant; being noticed a little increase in the partially saturated sample S80W50 in comparison with the completely dry sample S80W100.

5 Conclusions

1. The capillary-diffusive model proposed here describes the kinetics of the water absorption in GGBS mortars with enough accuracy. The kinetic coefficients such as sorptivity and diffusion coefficient should be previously determined in the fitting model process. The model describes the water absorption process for all times and allows us to know the contributions of the diffusion and capillary action in the water transport in mortars.
2. The variation of the % slag in the range 60-80% in materials with the same curing regime and preconditioning temperature doesn't influence considerably on the behavior of the materials. This is manifested in the little variation of the coefficients S and D .
3. The curing regime has important effects on the permeability of GGBS mortars. The mortars cured in water show best characteristics of impermeability (less S and D) that the mortars cured at open air.
4. The preconditioning temperature (for the same curing regime) is a factor that shows the influence of the saturation degree on the control of the water uptake. According with the S values, the samples preconditioning at 50°C show a less sorptivity in comparison with the samples preconditioning at 100°C .
5. The model proposed consider that the capillary sorption and diffusion are the principal mechanisms to the absorption of water in slag cement mortars but this don't consider for simplicity and for having a less contribution other mechanisms (such as permeation, osmosis, thermal migration, etc) that may be present in the uptake and movement of water in these materials. Future studies include the analysis of the possibility of existence (or not) of correlation effects between both, capillary and diffusive

process.

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Figure Captions

Figure 1. Scheme of the sorption test.

Figure 2. Cumulative water absorption for all cement mortars added with 60, 70 and 80% slag

Figure 3a. Cumulative water absorption for the sample S80W100 with 80% slag, curing in water and preconditioned at 100°C.

• Experimental — — Model

Figure 3b. Cumulative water absorption for the sample S70W100 with 70% slag, curing in water and preconditioned at 100°C.

• Experimental — — Model

Figure 3c. Cumulative water absorption for the sample S60W100 with 60% slag, curing in water and preconditioned at 100°C.

• Experimental — — Model

Figure 4. Cumulative water absorption for the sample S80A100 with 80% slag, curing at open air and preconditioned at 100°C.

• Experimental — — Model

Figure 5. Cumulative water absorption for the sample S80W50 with 80% slag, curing in water and preconditioned at 50°C.

● Experimental — Model













